Polymeric Hole-transporting Material with Flexible Backbone for Constructing Thermal-stable Inverted Perovskite Solar Cells

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1. Characterization

¹H NMR spectra was characterized via a Bruker-400 MHz spectrometer. Differential scanning calorimetry (DSC) was implemented on NETZSCH DSC 200 F3 differential scanning calorimeter with the scanning range from -35 °C to 300 °C at a rate of 10 °C min⁻¹ under N₂ atmosphere. Cyclic voltammetry measurement was constructed in Shanghai Chenghua chemical workstation using 0.1 M n-Bu₄NPF₆ dissolved in dichloromethane solution as electrolyte. During characterization, platinum was used as working electrode with Ag/AgCl as reference electrode, and Pt/C as counter electrode. UV-vis absorption spectra were recorded on a Shimadzu UV-2600 absorption spectrophotometer. Emission spectra was measured on a Hitachi F-4500 FL Spectrophotometer. The *J*–*V* curves were recorded with Shanghai Chenghua chemical workstation under an AM 1.5G illumination. The IPCE characteristics of the devices were measured with a self-built system of Qtest Station 2000. The Electrochemical impedance spectroscopy (EIS) measurement was constructed by using a ZHANER chemical workstation.

2. Device Fabrication

2.1 Materials.

Methylammonium iodide (MAI) and lead iodide (PbI₂, 99.99%) were purchased from Youxuan Tech (China). Phenyl-C₆₁-butyric acid methyl ester (PCBM), polytriarylamine (PTAA) and bathocuproine (BCP) (99.9%) were purchased from Xi'an p-OLED (China). The liquid reagents, including N, N-dimethylformamide (DMF, 99.8%), dimethyl sulfoxide (DMSO, 99.7%), isopropanol (IPA, 99.5%), and chlorobenzene (CB, 99.8%) were purchased from Sigma Aldrich.

2.2 Device Fabrication

The inverted perovskite solar cells (PSCs) were fabricated with a configuration of ITO/HTMs/MAPbI₃/PCBM/BCP/Ag.[1] The etched ITO substrates were cleaned with deionized water, acetone and IPA, sequentially, following with a treatment by UV-ozone for 30 min. The hole-transporting materials (HTMs) dissolved in chlorobenzene with a concentration of 5 mg·mL⁻¹ were spin-coated on the UV-ozone treated ITO substates. Perovskite precursor was prepared by mixing MAI (461 mg) and PbI₂ (159 mg) in a mixture solution of DMF (636 μ L) and dimethyl sulfoxide $(71\mu L)$, further stirred for 30 min at 60 °C. The perovskite layers were then fabricated using two-steps of spin-coating procedure. During the second step, 110 µL of CB was dripped on the substrates, following an annealing procedure at 100 °C for 10 min. Afterwards, PC₆₁BM solution in CB with a concentration of 20 mg mL⁻¹ was spincoated at perovskite surface at 3000 rpm for 30 s. The substrates were annealed at 100 °C for 10 min. Subsequently, BCP (0.5 mg·mL⁻¹ in isopropanol) was spin-coated as a buffer-layer at 4500 rpm. Finally, a 120 nm thickness of Ag contact was deposited on the top of BCP film using thermal evaporation.

3. Synthetic Procedures



Scheme S1. Synthetic routes for Z13.

3.1 Synthesis of compound Z5



Compound 1 (8.71 g, 19.61 mmol), compound 2 (19.5 g, 45.21 mmol) and $Pd(PPh_3)_4$ (680 mg, 0.588 mmol) were added into 200 mL tetrahydrofuran under N₂ atmosphere, then a solution of sodium carbonate (6.24 g, 58.87 mmol) in 30 mL water was added to the above mixture. The reaction was stirred for 8 hours. After the reaction was cooled to room temperature, the mixture was filtered and further extracted with ethyl acetate. The crude compound was purified through the silica gel

chromatography with petroleum ether and ethyl acetate as the eluent to give a white solid (11.5 g, yield: 66%).

1H NMR (400 MHz, DMSO-*d*₆) δ 9.30 (s, 2 H), 8.06 (s, 2 H), 7.90 (d, *J* = 9.0 Hz, 2 H), 7.56 (m, 4 H), 7.47 (d, *J* = 8.9 Hz, 2 H), 7.33 (d, *J* = 8.8 Hz, 2 H), 7.03 (m, 10 H), 6.97 (m, 8 H), 6.79 (m, 4 H), 3.74 (s, 12 H).

3.2 Synthesis of compound 3



Compound **Z5** (10.1 g, 11.31 mmol) and 1-(chloromethyl)-4-vinylbenzene (3.63 g, 23.78 mmol) were added to 75 mL anhydrous N,N-dimethylformamide. The reaction was cooled to 0 °C and stirred for 10 minutes. Then sodium hydride (2.25 g, 33.75 mmol, 60% in oil) was added into this mixture. The reaction was slowly warmed to room temperature and further stirred for 4 hours. The mixture was quenched with ice and extracted with Ethyl acetate. The crude compoud was purified by column chromatographyon silica gel with petroleum ether (PE) and EtOAc as eluent to afford a pale white powder (11.5 g, yield: 90.4%).

¹H NMR (400 MHz, DMSO-*d*₆) δ 8.14 (s, 2 H), 8.07 (d, *J* = 9.1 Hz, 2 H), 7.58 (m, 8 H), 7.22 (m, 4 H), 7.05 (m, 14 H), 6.89 (m, 8 H), 6.78 (m, 4 H), 6.61 (d, *J* = 17.6, 11.0 Hz, 2 H), 5.72 (d, *J* = 17.7 Hz, 2 H), 5.18 (m, 6 H), 3.74 (s, 12 H).

3.3 Synthesis of compound Z13



Compound **3** (1 g, 0.844 mmol) and 2,2'-Azoisobutyronitrile (5 mg, 0.03 mmol) were added to 2 mL toluene. The mixture was reacted under nitrogen atmosphere at 100 °C for 5 days. Then, the mixture was diluted with 3 mL dichloromethane, and recrystallized with ethyl acetate to give a light yellow solid (750 mg, yield: 75%).

 $M_{\rm n} = 6,842$, $M_{\rm w} = 11,091$, $M_{\rm w}/M_{\rm n} = 1.621$.

4. The calculated cost of compound Z13

Reagent	amount/ g	amount/ g amount/ mL price/ RMB g-1 or mL-1 / RMB					
Z5	1	1 NA 138.85 138.85					
1-(chloromethyl)- 4-vinylbenzene	0.36	0.22					
NaH	0.112	NA	0.4	0.04	0.01		
DMF	NA	0.02					
Ethyl acetate	NA	NA 50 0.1 5					
Petroleum ether	NA	NA 1000 0.1 100					
Total price		23.12					
Amount of compound 3		NA					
Price of compound 3		213 RMB g-1					

Table S1 The calculated cost of compound **3**.

Reagent	amount/ g	amount/ g amount/ price/ RMB Total mL g-1 or mL-1 / RMB				
Compound 3	1	NA	213	213	33.00	
AIBN	0.005	NA	0.4	0.002	0.00	
Toluene	NA	0.5	0.05	0.025	0.01	
Dichloromethane	NA	0.08				
Ethyl acetate	NA	NA 50 0.1 5				
Total price		\$33.85				
Amount of Z13		NA				
Price of Z13		\$45.12 g ⁻¹				

Table S2 The calculated cost of Z13

5 Results



Fig. S1 Cyclic voltammetry curve of ferrocene in a CH₂Cl₂ solution.

Table 55 Electrochemical parameters of firms.						
HTMs	$E_{\rm ox}{}^{\rm a}$	$E_{\rm red}{}^{\rm b}$	$E_{\rm or}{}^c$	E^{d}	ΔE^{e}	$E_{\rm HOMO}^{\rm f}$
Ferrocene	0.66	0.37	0.515	0.63	-0.115	
Z5	0.75	0.64	0.695			0.810
Z13	0.77	0.62	0.695			0.810

Table S3	Electrochemical	parameters	of HTMs
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^a E_{ox} represents the oxidation potiential; ^b E_{red} represents the reduction potiential; ^c E_{or} represents the measured oxidation-reduction potiential, $E_{or} = (E_{ox} + E_{red})/2$;

^d E^{d} represents the standard oxidation-reduction potiential of ferrocene/ferrocenium (Fc/Fc⁺) with respect to the Ag/Ag⁺;

 $e\Delta E^{e}$ represents the difference between the measured potiential and standard data of

ferrocene/ferrocenium (Fc/Fc⁺). ^f E_{HOMO} represents the standardized values.



Fig. S2 TGA measurement of Z13.



Fig. S3 *J-V* curves measured by forward and reverse scan, respectively.



Fig. S4 Equivalent circuit to fit the electrochemical impedance spectroscopy.

Sample	$\tau_{l}(ns)$	τ_2 (ns)	A ₁ (%)	$A_{2}(\%)$
Perovskite	16.6	114.0	89	11
Z13	14.7	80.9	96	4
Z5	16.0	100.4	98	2

	PTAA	15.8	78.9	86	14
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НТМ	number	$V_{\rm oc}$ /V	$J_{\rm sc}$ /mA cm ⁻ 2	<i>PCE /</i> %	FF
Z5	1	1.053	21.94	17.83	0.77
	2	1.049	22.18	17.82	0.77
	3	1.058	22.27	17.57	0.75
	4	1.041	22.62	17.38	0.74
	5	1.062	22.32	17.29	0.73
	6	1.039	22.35	17.87	0.77
	7	1.047	21.95	17.32	0.75
	8	1.039	21.90	17.71	0.78
	9	1.038	21.97	17.55	0.77
	10	1.038	21.99	17.65	0.77
	11	1.046	21.94	17.54	0.76
	12	1.053	22.29	18.05	0.77
	13	1.046	21.53	17.51	0.78
	14	1.055	22.36	17.81	0.76
	15	1.039	22.03	17.35	0.76
	Average	1.047 ± 0.008	22.11±0.27	17.62 ± 0.23	0.76 ± 0.01

 Table S5 Photovoltaic parameters of repeated test in Z5-based inverted PSCs.

Table S6 Photovoltaic parameters of repeated test in Z13-based inverted PSCs.

НТМ	number	V _{oc} /V	$J_{\rm sc}$ /mA cm ⁻ 2	PCE /%	FF
Z13	1	1.042	22.42	17.70	0.76
	2	1.047	22.48	17.53	0.74
	3	1.035	22.68	17.57	0.75
	4	1.049	22.70	17.60	0.74
	5	1.058	22.38	17.96	0.76
	6	1.075	22.25	17.64	0.74
	7	1.069	22.43	17.38	0.72
	8	1.076	22.61	17.57	0.72
	9	1.071	22.46	17.69	0.74
	10	1.068	22.55	17.57	0.73
	11	1.087	22.48	18.62	0.76
	12	1.082	22.44	18.19	0.75
	13	1.080	22.37	18.57	0.77
	14	1.081	22.45	18.49	0.76
	15	1.085	22.59	17.81	0.73
	Average	1.067 ± 0.016	22.48±0.13	17.86 ± 0.40	0.75 ± 0.01

HTM	number	$V_{\rm oc}$ /V	$J_{\rm sc}$ /mA cm ⁻ 2	PCE /%	FF
PTAA	1	1.057	22.41	17.54	0.74
	2	1.045	21.61	16.17	0.72
	3	1.057	22.20	16.63	0.71
	4	1.065	22.27	17.26	0.73
	5	1.047	22.01	17.82	0.77
	6	1.038	22.06	17.07	0.75
	7	1.043	22.02	16.12	0.70
	8	1.053	22.12	17.88	0.77
	9	1.046	22.00	15.94	0.69
	10	1.040	22.44	18.19	0.78
	11	1.044	22.30	18.01	0.77
	12	1.077	22.26	18.64	0.78
	13	1.079	22.32	18.75	0.78
	14	1.039	22.28	17.95	0.78
	15	1.045	22.02	17.44	0.76
	Average	1.052 ± 0.013	22.15±0.20	17.43 ± 0.86	0.75 ± 0.03

Table S7 Photovoltaic parameters of repeated test in PTAA -based inverted PSCs.



Fig. S7 ¹H NMR spectrum of compound Z5 (DMSO- d_6)



Fig. S8 ¹H NMR spectrum of compound 3 (DMSO- d_6)

6 References

[1] Y. Lu, X. Zong, Y. Wang, W. Zhang, Q. Wu, M. Liang, S. Xue, Noncovalent functionalization of hole-transport materials with multi-walled carbon nanotubes for stable inverted perovskite solar cells. *Journal of Materials Chemistry C*, 7 (2019) 14306-14313.